

NON-LINEAR WAVES IN FLUIDS NEAR THE CRITICAL POINT

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A non linear model associated with a Landau-Ginzburg-like behavior in mean field approximation forecasts phase transition waves and solitary kinks near the critical point. The behavior of isothermal waves is different of the one of isentropic waves as well in conservative cases as in dissipative cases.

1. Introduction

The study of plane waves propagating in fluid second gradient theory is a main subject in continuum mechanics^{1–7}. From our paper⁽⁸⁾ where strong variation of density for the matter constituent occurs in isothermal conservative motions, we propose an extension to other thermodynamical conditions and for dissipative motions. Such cases appear in phase transitions through interfacial layers^{9,10}. Near the critical point the thickness of the interface separating the two phases of a fluid gets non molecular dimension. The theory of second gradient corresponding to an extended van der Waals model with thermodynamical potentials modeling the mean field approximation allows to study the interface in equilibrium^{11,12}. With a convenient rescaling, the governing equations of material waves can be expressed for conservative and viscous motions with a Landau-Ginzburg-like behaviour¹³; they are compatible with the second law of thermodynamics and we can rewrite the one-dimensional equations of non homogeneous fluids in terms of density^{14,15}. To obtain wave motions, we study the thermodynamical potentials of a fluid near the critical point and extend the expression given in^{9,10} to the local internal energy. Thermodynamical potentials are introduced in equation of motions in two cases: when the temperature is fixed (isothermal motions) and when the specific entropy along trajectories is constant (isentropic motions). We find the possibility

of non-linear waves in form of solitary waves or phase transition waves for conservative motions, but no kinks as traveling waves can appear for non conservative motions. Finally we discuss the fluid velocity near the critical point depending on the boundary conditions.

2. Thermodynamic potentials near the critical point

In mean field approximation, the thermodynamical potentials of fluids can be expressed in an analytical form near the critical point¹⁰. The chemical potential of a homogeneous fluid can be written in the following form^{9,16}

$$\mu = \mu^c + \mu_{01}^c (T - T_c) + \mu_{11}^c (\rho - \rho_c) (T - T_c) + \frac{1}{6} \mu_{30}^c (\rho - \rho_c)^3 \quad (1)$$

where $\rho - \rho_c$ and $T - T_c$ denote the difference between the density ρ and the Kelvin temperature T from their values ρ_c, T_c at the critical point. This simple expansion depends on coefficients corresponding to the values of the partial derivatives of μ at the critical point; that is to say,

$$\mu_{ij}^c = \frac{\partial^{i+j} \mu}{\partial \rho^i \partial T^j} (\rho_c, T_c)$$

The chemical potential μ has been expanded using a cubic polynomial in terms of density and temperature; they are not the natural variables but the most convenient for the calculations.

Denoting the coefficients by $A \equiv \mu_{11}^c > 0$, $B \equiv \frac{1}{6} \mu_{30}^c > 0$ (the sign conditions are at the critical point) and $\mu_o \equiv \mu^c + \mu_{01}^c (T - T_c)$ depending only on T , Eq. (1) reads

$$\mu = \mu_o - A(T_c - T)(\rho - \rho_c) + B(\rho - \rho_c)^3 \quad (2)$$

Expression (2) allows us to solve the problems of waves in an universal way where $T - T_c$ plays the role of an order parameter. Such a chemical potential expansion agrees with the van der Waals equation of state¹¹ where only the values A and B are representative of a particular fluid.

Consequently, the free energy per unit volume ψ can be written in the form

$$\psi = \mu_o \rho - \frac{A}{2} (T_c - T)(\rho - \rho_c)^2 + \frac{B}{4} (\rho - \rho_c)^4 - f(T) \quad (3)$$

where f is an additive function of T only. The pressure p verifies $p = \rho\mu - \psi$ and we get near ρ_c the expansion

$$p = p_c + D(T - T_c) - (v - v_c) \left(A_1(T - T_c) + B_1(v - v_c) \right) \quad (4)$$

where $v = \frac{1}{\rho}$ denotes the specific volume, $D = \frac{\partial p}{\partial T}(v_c, T_c)$, $f(T_c) = p_c$ and $A_1 = A \rho_c^3$, $B_1 = B \rho_c^7$.

Due to the general properties of two-phase regions near the critical point the two-density version of specific internal energy of the fluid is expressible in the form ¹⁰

$$\alpha(v, s) = (x^2 - y)^2 + y^2 + \beta x + \gamma y + \delta \quad (5)$$

with $x = ar + b\sigma$, $y = cr + d\sigma$ where $r = v - v_c$, $\sigma = s - s_c$, $\beta, \gamma, \delta, a, b, c, d$ are constants and s denotes the specific entropy of the fluid. Taking into account that $p = -\frac{\partial \alpha}{\partial v}(v, s)$, $T = \frac{\partial \alpha}{\partial s}(v, s)$ and denoting $\alpha_1(v, s) \equiv \alpha(v, s) + p_c(v - v_c) - T_c(s - s_c) - \frac{B_1}{4}r^4$, we obtain the partial differential equation

$$\frac{\partial \alpha_1}{\partial r} + (D - A_1 r) \frac{\partial \alpha_1}{\partial \sigma} = 0$$

which yields the general solution for the specific internal energy

$$\alpha = g(\sigma - Dr + \frac{A_1}{2}r^2) + B_1 \frac{r^4}{4} - p_c r + T_c \sigma$$

Due to the fact that α must verify the general form (5), $g(u)$ is necessarily a polynomial with respect to $u = \sigma - Dr + \frac{A_1}{2}r^2$ in the form $g(u) = Eu + Gu^2$. The term Gu^2 yields a term of four degree in r and r must be a function of x only. No term in the form xy appears in (5); consequently $\sigma - Dr$ does not contain the variable y and the general form of α is

$$\alpha = E(k_2 y + \frac{A_1}{2} k_1^2 x^2) + G(k_2 y + \frac{A_1}{2} k_1^2 x^2)^2 + \frac{B_1}{4} k_1^4 x^4 - p_c r + T_c \sigma$$

where E and G are two constants.

By straightforward calculations, an identification with the expression (5) yields the general expression for the specific internal energy

$$\alpha(v, s) = x^4 - 2x^2 y + 2y^2 - p_c(v - v_c) + T_c(s - s_c) \quad (6)$$

$$\text{with } x = \sqrt[4]{\frac{B_1}{2}} (v - v_c) \text{ and } y = \frac{1}{A_1} \sqrt{\frac{B_1}{2}} [D(v - v_c) - (s - s_c)]$$

As a consequence the pressure gets the form

$$p = p_c + 4 \sqrt[4]{\frac{B_1}{2}} (y - x^2) x + \frac{D}{A_1} \sqrt{2B_1} (x^2 - 2y) \quad (7)$$

and in the case where s is constant, the specific enthalpy reduces to the form

$$h = \frac{DB_1}{A_1} v_c^3 \left(v_c^2 (\rho - \rho_c)^2 + \frac{2D}{A_1} (\rho - \rho_c) \right) + h_o \quad (8)$$

where h_o is a constant depending on s .

Near the critical point, a fluid behaves like a gas but with a high density¹⁷. As for interfaces separating two bulks, the fluid is not homogeneous. The view that a non-homogeneous fluid near its critical point may be treated as matter in bulk with a local energy density that is that of a hypothetically uniform fluid of composition equal to the local composition with an additional term arising from the non-uniformity, and that the latter may be approximated by a gradient expansion typically truncated in second order is most likely to be successful and perhaps even qualitatively accurate^{10,18}. The first study has been done on the theory of the near-critical interface within the framework of the van der Waals theory of capillarity⁹; the simplest model able to take into account the density and its gradient uses a unique supplementary quantity represented by the constant C of internal capillarity. In S.I. units, the value of C for water at 20° Celsius is of the order of 10^{-16} (see¹⁵). In the mean field approximation the expression of the internal energy α_{nh} of a non homogeneous fluid near the critical point is in the form^{10,12,14}

$$\alpha_{nh} = \alpha + \frac{C}{2} (\nabla \rho)^2$$

The supplementary term due to the non-homogeneity of the medium in the expression of the internal energy is effective only in interfaces and for fluids near the critical point.

3. Motions of a fluid near the critical point

Equations of motions are classically given in the literature with the additive *second gradient term*^{6,8}. Fluid motions are associated in the literature with the *capillary fluid equation of motion*¹⁴:

$$\rho \mathbf{\Gamma} + \nabla p + \rho \nabla (\Omega - C \nabla^2 \rho) - \text{div } \sigma_v = 0 \quad (9)$$

where p is the previous thermodynamic pressure associated with the medium considered as homogeneous, (i.e. the pressure entering in the thermodynamic potentials of the homogeneous fluid near the critical point), Ω is the body force potential, $\sigma_v = \lambda \text{tr}(\Delta) Id + 2\mu \Delta$ is the viscous stress tensor in the classical form where Δ is the velocity deformation tensor,

Γ the acceleration vector, ∇ the gradient operator and ∇^2 the Laplacian operator. The mass balance yields

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho \mathbf{V} = 0 \quad (10)$$

where \mathbf{V} denotes the velocity of the fluid.

Let us notice that we can obtain the equation of energy such that the system is compatible with the second law of thermodynamics^{19,20}. Capillary fluids belong to the class of dispersive systems because the internal energy depends not only on density but also on its derivatives with respect to space variables; we have previously seen that the constant solutions are nevertheless stable²¹.

Let us study the one-dimensional problem when the velocity V and the density ρ are only functions of the variable $\zeta = z - ct$, where z is the space variable, t the time and c the wave celerity with respect to a Galilean frame:

$$V = V(z - ct), \quad \rho = \rho(z - ct)$$

The mass balance equation yields

$$-c \frac{d\rho}{d\zeta} + \frac{d(\rho V)}{d\zeta} = 0$$

and by integrating, we obtain

$$\rho(V - c) = q \quad (11)$$

where q is constant in the motion. In the cases of waves we obtain

$$\Gamma = \frac{1}{2} \frac{d}{d\zeta} (V - c)^2$$

We consider that body forces are negligible as in space with weightlessness. In the uni-dimensional case,

$$\operatorname{div} \sigma_v = (\lambda + 2\mu) q \frac{d^2}{d\zeta^2} \left(\frac{1}{\rho} \right)$$

In the following, we assume that $\nu = (\lambda + 2\mu)/\rho$ is constant in the fluid as assumed in interfaces¹⁷. Then Eq. (9) yields

$$\frac{d}{d\zeta} \left(\frac{1}{2} \frac{q^2}{\rho^2} - C \frac{d^2 \rho}{d\zeta^2} - \nu q \frac{d}{d\zeta} \left(\frac{1}{\rho} \right) + \frac{1}{\rho} \frac{dp}{d\zeta} \right) = 0$$

We consider two cases *a*) isothermal motions corresponding to fluid motions near equilibrium conditions and *b*) isentropic motions corresponding to fast velocities. In the two cases, we can write $\frac{1}{\rho} \frac{dp}{d\zeta} = \frac{dH}{d\zeta}$ where H is the

chemical potential of the fluid in case *a*) and the specific enthalpy in case *b*). In all the cases, near the critical point $\rho \approx \rho_c$; consequently $\nu q/\rho^2 \approx \nu q/\rho_c^2$ and the equation of motion becomes

$$C \frac{d^2 \rho}{d\zeta^2} - \frac{\nu q}{\rho_c^2} \frac{d\rho}{d\zeta} = H - H_o + \frac{1}{2} \frac{q^2}{\rho^2} \quad (12)$$

where H_o is constant.

4. Example of waves of a fluid near the critical point

Two main cases are generally considered for traveling waves : isothermal processes and isentropic processes. Motions can be conservative as a mathematical limit of the dissipative case. Nevertheless, in thin interfaces the viscosity may be neglected and conservative cases may be considered as realistic physically²². The cases of viscous fluid involve inequality due to Liapounov functions.

4.1. Existence of solitary waves

Let us notice that for viscous capillary fluid, solitary waves as kinks cannot appear. Multiplying Eq. (12) by $\frac{d\rho}{d\zeta}$ we obtain by integration :

$$\frac{C}{2} \left(\frac{d\rho}{d\zeta} \right)^2 - K(\rho) + \frac{1}{2} \frac{q^2}{\rho} = \int_{\zeta_o}^{\zeta} \frac{\nu q}{\rho_c^2} \left(\frac{d\rho}{d\zeta} \right)^2 d\zeta \quad (13)$$

where ζ_o is a constant and $K'(\rho) = H(\rho) - H_o$.

Eq. (13) allows to obtain a first integral only when $\nu = 0$. Due to the fact that

$$\text{for } \nu > 0 \text{ and } \zeta > \zeta_o, \quad \int_{\zeta_o}^{\zeta} \frac{\nu q}{\rho_c^2} \left(\frac{d\rho}{d\zeta} \right)^2 d\zeta > 0$$

it is not possible to obtain $\rho(-\infty) = \rho(+\infty)$ and no solitary wave can appear in dissipative motions.

4.2. Isothermal waves

In the isothermal case the wave motion is obtained by using the chemical potential μ given by Eq. (2)

$$\frac{1}{2} \frac{d^2 \rho}{d\zeta^2} - \frac{\nu q}{2 \rho_c^2 C} \frac{d\rho}{d\zeta} = -\frac{A}{2C} (T_c - T) (\rho - \rho_c) + \frac{B}{2C} (\rho - \rho_c)^3 + \frac{q^2}{4C \rho^2} + k_o \quad (14)$$

where k_o is a constant.

Near the critical point $|(\rho - \rho_c)/\rho_c| \ll 1$; consequently, we get the following expansion to the second order in $(\rho - \rho_c)/\rho_c$

$$\frac{1}{\rho^2} \approx \frac{1}{\rho_c^2} \left(1 - \frac{2(\rho - \rho_c)}{\rho_c} + \frac{3(\rho - \rho_c)^2}{\rho_c^2} \right)$$

and to the fourth order Eq. (14) yields

$$\begin{aligned} \frac{1}{2} \frac{d^2 \rho}{d\zeta^2} - \frac{\nu q}{2\rho_c^2 C} \frac{d\rho}{d\zeta} &= \frac{B}{2C} \left(\rho - \rho_c + \frac{q^2}{2B\rho_c^4} \right)^3 \\ &\quad - \frac{1}{2C} \left(A(T_c - T) + \frac{q^2}{\rho_c^3} \right) + \left(\rho - \rho_c + \frac{q^2}{2B\rho_c^4} \right) + k_1 \end{aligned}$$

where k_1 is constant. We define the following change of variables:

$$\rho = \left(\rho_c - \frac{q^2}{2B\rho_c^4} \right) (1 + \varepsilon Y), \quad \zeta = L \xi \quad \text{and} \quad Q = \frac{q \left(A(T_c - T) + \frac{q^2}{\rho_c^3} \right)}{(2C)^{3/2} B^{1/2} \rho_c^2} \quad (15)$$

$$\text{with } L^2 = \frac{2C}{A(T_c - T) + \frac{q^2}{\rho_c^3}} \quad \text{and} \quad \varepsilon^2 = \frac{A(T_c - T) + \frac{q^2}{\rho_c^3}}{B \left(\rho_c - \frac{q^2}{2B\rho_c^4} \right)^2}$$

Then, the equation of isothermal waves writes

$$\frac{1}{2} \frac{d^2 Y}{d\xi^2} - \nu Q \frac{dY}{d\xi} = Y^3 - Y + k_1 \quad (16)$$

Conservative case, $\nu = 0$: we obtain the first integral

$$\left(\frac{dY}{d\xi} \right)^2 = (1 - Y^2)^2 - a_1 Y - b_1 \quad (17)$$

where a_1 and b_1 are two constants. The intersections of the straight line $a_1 Y + b_1$ and of the quartic $(1 - Y^2)^2$ yield the density range

Interfacial propagation - We recall the main results of ⁽⁸⁾: in the bulks phases, the densities are constant and thus the first and second derivatives of Y are zero. The straight line is tangent to the quartic at the associated points. If the bulk phases are different on both sides of the interface, the straight line has to be bitangential to the quartic which implies a_1 and b_1 are null (case of two phases). A liquid-vapor interface wave is similar to the one obtained in the equilibrium case ($q = 0$) but mass flows through the

interface. Vaporization or condensation phenomena depend on the sign of q . This case corresponds to a shock wave in the sense of Slemrod ² and

$$\rho = \left(\rho_c - \frac{q^2}{2B\rho_c^4} \right) \left(1 + \varepsilon \tanh \left(\frac{\zeta}{L} \right) \right) \quad (18)$$

(see left side of fig. 1).

Solitary waves - It is also possible to obtain a solitary wave moving in one of the bulk phases (liquid or vapor). The straight line is tangent to the quartic at the point associated with the bulk $Y = Y_o$ and intersect the quartic at the point associated with the *middle* of the wave $Y = Y'_o$. When Y belongs to the interval between Y_o and Y'_o , the right hand side of Eq. (17) must be positive and this authorizes only two possibilities:

- a) $-1 < Y_o < -1/\sqrt{3}$ and $Y_o < Y'_o < 1$, the density increases in the wave (see right side of fig. 1),
- b) $1/\sqrt{3} < Y_o < 1$ and $-1 < Y'_o < Y_o$, the density decreases in the wave.

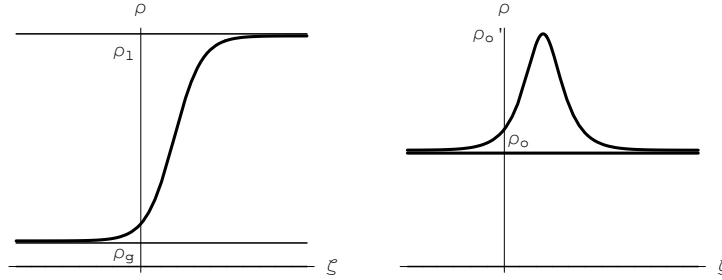


Figure 1. On the left side of the figure a phase transition wave is represented (densities ρ_l and ρ_g are associated with the liquid and vapor bulks); on the right side a traveling wave is a kink associated with case a) (density ρ_o corresponds to the bulk of the fluid).

Consequences - The change of variables (15) assumes that $T_c - T + \frac{q^2}{A\rho_c^3}$ is positive; Then, for $T > T_c$ the flow through the interface must be more important than the limit $q_m = \sqrt{A\rho_c^3(T - T_c)}$ and the wave velocity ℓ must be greater than the limiting value $\ell_m = \sqrt{A\rho_c(T - T_c)}$ which is the celerity of isothermal acoustic waves.

Dissipative case, $\nu > 0$: In this case no solitary wave appears (see

section 4.1). Let us define $Z(Y) = \frac{dY}{d\xi}$; then Eq. (16) yields

$$\frac{1}{2} Z Z' - \nu Q Z = Y^3 - Y + k_1$$

We look for the phase transition waves with a solution in the form

$$Z(Y) = \alpha_1 Y^2 + \beta_1 Y + \gamma_1$$

where the polynomial $\alpha_1 Y^2 + \beta_1 Y + \gamma_1$ has two real roots. Then, the differential equation

$$\frac{dY}{d\xi} = \alpha_1 Y^2 + \beta_1 Y + \gamma_1$$

has a solution in the same form than (18); (see left side of fig. 1). Straightforward calculations prove that the polynomial has two real roots when

$$\nu^2 q^2 \left(A(T_c - T) + \frac{q^2}{\rho_c^3} \right) \leq 24 C^3 B \rho_c^4$$

which corresponds to a velocity q/ρ_c of the wave small enough. This condition does not appear in the conservative case where $\nu = 0$.

4.3. Isentropic waves

For an isentropic conservative motion, $s = Cte$ and the equation of motion is in a form deduced from Eq. (12),

$$C \frac{d^2 \rho}{d\zeta^2} = h - h_o + \frac{1}{2} \frac{q^2}{\rho^2}$$

where h is now the specific enthalpy. We consider the new change of variables

$$\rho = \rho_c (1 + Y), \quad \xi = L \zeta \quad \text{and} \quad q = b Q$$

with

$$L^2 = \frac{2 C \rho_c^4 A_1}{D B_1}, \quad b^2 = \frac{D B_1}{\rho_c A_1}$$

and the equation of wave motions yields

$$\frac{1}{4} \left(\frac{dY}{d\xi} \right)^2 = \frac{Y^3}{3} (1 + 3 Q^2) + \frac{Y^2}{2} (\tau - 2 Q^2) + a_o Y + b_o \quad (19)$$

with $\tau = \frac{2\rho_c D}{A_1}$ and a_o and b_o are two constants. We denote by $\ell_m = \frac{2D^2 B_1}{A_1^2} v_c^2$ a limit celerity of the waves with respect to the fluid. Due to the form of the second member of Eq. (19), we notice immediately that it is not possible to obtain phase transition waves. Consequently traveling waves cannot appear in dissipative motions when the entropy is constant in the fluid. The two cases are represented on fig 2.

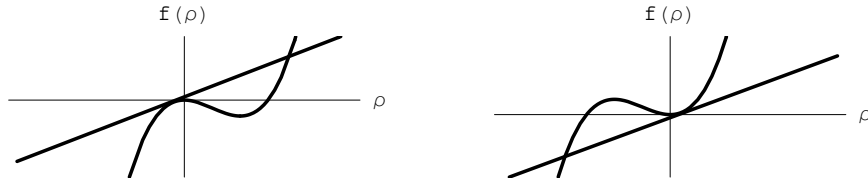


Figure 2. On the left side of the figure, the case where the line $f(Y) = a_o Y + b_o$ is above the cubic representing the left side of Eq. (19) is presented; on the right side the opposite situation: the line $f(Y) = a_o Y + b_o$ is below the cubic.

Case 1: $Q^2 < \tau/2$ or $\ell < \ell_m$. In this case solitary waves cannot appear (see left side of fig 2).

Case 2: $Q^2 > \tau/2$ or $\ell > \ell_m$. In this case solitary waves are possible depending on initial conditions (see right side of fig 2).

In the van der Waals model of pressure we obtain by straightforward calculations

$$D = \frac{4p_c}{T_c}, \quad A_1 = \frac{6p_c \rho_c}{T_c}, \quad B_1 = \frac{3p_c \rho_c^3}{2}$$

and consequently, $\ell_m = \sqrt{\frac{4}{3} \frac{p_c}{\rho_c}}$.

4.4. Fluid velocity near the critical point

For a given density, the fluid velocity is deduced at time $t = 0$ from Eq. (11). Consequently,

$$V(z) = c + \frac{q}{\rho(z)}$$

where $V(z)$ is the fluid velocity at z and c is an arbitrary constant. At any time t ,

$$V(z - ct) = c + \frac{q}{\rho(z - ct)}$$

where initial conditions yield the arbitrary velocity c .

Interface propagation - In a phase transition wave, the fluid changes from liquid to vapor as its volume increases. Consequently such a phenomenon cannot occur in a closed tube but only in a tube with only one closed end. For example, the tube is closed at the other end with a piston whose displacement is imposed. The fluid velocity at the fixed end is zero (for example liquid bulk) and $c = -q/\rho_l$. If we impose a value U for the piston velocity in the vapor bulk, we deduce the value of q

$$q \left(\frac{1}{\rho_v} - \frac{1}{\rho_l} \right) = U$$

where ρ_v and ρ_l are the values of the density in the vapor and liquid bulks. From the values of ρ_v and ρ_l deduced from expression (18), we determine the flow q and the velocities $\ell \simeq q/\rho_c$ and c .

Solitary wave - The volume of the interface that moves in only one bulk phase is constant. Such a wave may be moving in a closed tube such as Natterer tube²³. At the ends (assumed far from the region of the wave) the velocity in the bulk phase is zero and $c \simeq -q/\rho_c$. When the temperature is close to T_c , the model of fluid endowed with internal capillarity allows to obtain traveling waves in a tube which depends on two arbitrary parameters.

5. Conclusion

The mean field approximation for fluid near the critical point is able to predict solitons and transition of phase waves. Two kinds of waves are investigated: *a)* liquid-vapor waves in the case of isothermal medium whose the celerity depends on the distance between the temperature and its critical value. Above the critical temperature, the fluid behaves like an elastic medium and the waves are supersonic with respect to the isothermal sound velocity⁸. Below the critical temperature, the fluid behaves like a nonrigid medium and the wave velocities can take any value in conservative motion but are bounded in dissipative motion proportionally to the viscosity of the fluid. *b)* Traveling kinks appear in the conservative case as well as for isothermal than for isentropic motions.

Thermodynamics functions and parameters vanish or diverge at the critical point proportionally to some power of the distance from that point currently measured as $T - T_c$. The critical exponents are central to the discussion of critical phenomena and can be generalized by nonclassical value of critical point exponents for the potentials given in section 2. The problem can be extended for multi-component fluid mixtures but critical points are not unique; for a mixture of fluids there is a curve of critical points.

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